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(54) SURFACE TREATED METAL MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a rust-preventive coating film having equivalent functions to those of a chromated film without using hexavalent chromium by forming a chemical conversion film essentially comprising an oxo-acid compd. or an oxo-acid hydrogen compd. of a rare earth element and/or a group IV element.

SOLUTION: The oxo-acid compd. or oxo-acid hydrogen compd. of a rare earth element/a group IV element to be used is a compd. of an oxidized anion such as phosphoric acid ion, tungstic acid ion and vanadic acid ion and Y, La, Se, Zn, and the oxo-acid hydrogen compd. means a compd. containing hydrogen as a part of a cation. The compd. is prepared as particles having $\leq 3 \mu\text{m}$, preferably $\leq 2 \mu\text{m}$ average particle size, and is dispersed together with a resin and an org. inhibitor in a solvent in a colloidal state to obtain a treating liquid. The obtd. treating liquid is applied on a metal sheet, dried, and heat treated at 100 to 200°C to form a rust-preventive film. It is enough when the amt. of the oxo-acid compd. or oxo-acid hydrogen compd. of the rare earth element/the group IV element is $\geq 1 \text{ mg/m}^2$ calculated as the rare earth element/the group IV element.

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CLAIMS

[Claim(s)]

[Claim 1] The oxygen acid compound of rare earth elements and/or an IVA group element, the oxygen acid hydride, or the surface treatment metallic material characterized by having the corrosion-resistant enveloping layer which uses these mixture and resin as a principal component.

[Claim 2] The surface treatment metallic material according to claim 1 rare earth elements and/or whose IVA group element are an yttrium, a lanthanum, a cerium, and/or a zirconium.

[Claim 3] Claim 1, the surface treatment metallic material of two publications whose anion kinds of an oxygen acid compound are a phosphate anion, tungstic-acid ion, molybdic-acid ion, and/or vanadium acid ion.

[Claim 4] The surface treatment metallic material according to claim 3 a phosphoric acid compound and whose phosphoric acid hydride are alt.(hydrogen) phosphoric acid, a metaphosphoric acid compound, polyphosphoric acid (hydrogen) compounds, or such mixture.

[Claim 5] The surface treatment metallic material according to claim 1 to 4 which contains one sort or two sorts or more of compounds with which a corrosion-resistant enveloping layer is chosen from the oxide, the hydroxide, halogenide, and organic-acid compound of rare earth elements as an addition component.

[Claim 6] The surface treatment metallic material according to claim 5 whose rare earth elements of an addition component are ceriums.

[Claim 7] The surface treatment metallic material according to claim 1 to 6 with which a corrosion-resistant enveloping layer contains organic system inhibitor as an addition component.

[Claim 8] Organic system inhibitor The formylation derivative of an N-phenyl-dimethyl pyrrole, The thioglycolic acid ester expressed with $\text{HS-CH}_2\text{COOC}_n\text{H}_{2n+1}$ (n is the integer of 1-25), and its derivative, alpha-mercapto carboxylic acid expressed with $\text{C}_n\text{H}_{2n}(\text{SH})\text{COOH}$ (n is the integer of 1-25), and its derivative, A quinoline and its derivative, triazine dithiol and its derivative, gallate, and its derivative, The surface treatment metallic material according to claim 7 which are one sort or two sorts or more-of mixture chosen from a nicotinic acid and its derivative, a catechol and its derivative, and/or a conductive polymer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the surface treatment metallic material which has the enveloping layer which there is processing flattery nature, and is excellent in corrosion resistance, and does not contain hexavalent chromium at all.

[0002]

[Description of the Prior Art] In order to give rust-proofing nature conventionally to the cold rolled sheet steel used for the application of an automobile, home electronics, building materials, etc., a galvanized steel sheet and a zinc system alloy-plating steel plate, an aluminum plating steel plate, etc., generally covering a chromate film on those front faces is performed. As this chromate treatment, there are an electrolytic type chromate and a spreading mold chromate. The electrolysis chromate used the chromic acid as the principal component, and has been performed by carrying out cathode electrolysis processing of the metal plate using the bath which otherwise added various anions, such as a sulfuric acid, phosphoric acid, boric acid, and a halogen. Moreover, it has been carried out by a spreading mold chromate having the problem of the elution of the chromium from a chromate treatment metal plate, adding inorganic colloid and an inorganic anion in the solution which returned a part of hexavalent chromium to trivalent beforehand, or the solution which specified hexavalent chromium and a chromium ratio, considering as processing liquid, immersing a metal plate into it or carrying out the spray of the processing liquid to a metal plate.

[0003] Although the chromate film formed of electrolysis among chromate films has little elution nature of hexavalent chromium, it cannot say that anti-corrosiveness is enough, but especially, when the coat damages at the time of processing etc. are large, the corrosion resistance falls. On the other hand, although the corrosion resistance of the metal plate covered with the spreading mold chromate film is high and being excelled especially in processing section corrosion resistance, the elution of the hexavalent chromium from a chromate film poses a problem greatly. If an organic polymer is covered, although the elution of hexavalent chromium is controlled considerably, it is not enough. Moreover, by approach which is indicated by JP,5-230666,A and which is generally called a resin chromate, although an improvement is found by elution control of hexavalent chromium, the elution of a minute amount is not avoided. Thus, in order to stop the elution of hexavalent chromium completely, development of the rust-proofing sex skin film which has a function equivalent to the chromate film which contains the conventional hexavalent chromium, not using hexavalent chromium at all is needed.

[0004] We considered as the general-purpose chemical conversion coat which does not contain at all the hexavalent chromium replaced with the present chromate treatment as indicated to PCT/JP 97/00272, and got the enveloping layer with the oxygen acid (hydrogen) compound of rare earth elements. While giving processing flattery nature as the shape of a paste by using a lanthanum and a cerium as a phosphoric acid compound as the example and controlling corrosion according to the barrier effectiveness, control of a cathodic reaction and the inorganic system corrosion resistance chemical conversion coat which controls an anodic reaction by the passivation of a phosphate coating mold and

the passivation of a mill-scale mold by making phosphoric acid superfluous further were obtained with cerium ion.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is by making the inorganic system chemical conversion coat excellent in the corrosion resistance which does not use above-mentioned hexavalent chromium at all contain resin to offer the new technique about the surface treatment metallic material which has the coat which strengthened processing flattery nature and corrosion resistance.

[0006]

[Means for Solving the Problem] That the general-purpose chemical conversion coat replaced with the present chromate treatment should be designed by the system which does not contain hexavalent chromium at all, this invention persons become possible [obtaining new and epoch-making inorganic and organic system chemical conversion coat formed with the oxygen acid acid compound of rare earth elements and/or an IVA group element, oxygen acid hydride or such mixture, and resin], as a result of repeating examination wholeheartedly. Organic system inhibitor and/or a cerium compound are made to contain in an enveloping layer furthermore, and corrosion control is complemented and strengthened.

[0007] The place made into the summary of the invention is a surface treatment metallic material characterized by having the corrosion-resistant enveloping layer which uses the oxygen acid compound of (1) rare earth elements and/or an IVA group element, oxygen acid hydride or such mixture, and resin as a principal component.

(2) The surface treatment metallic material of the aforementioned (1) publication rare earth elements and/or whose IVA group element are an yttrium, a lanthanum, a cerium, and/or a zirconium.

(3) The above (1), the surface treatment metallic material given in (2) whose anion kinds of an oxygen acid compound are a phosphate anion, tungstic-acid ion, molybdic-acid ion, and/or vanadium acid ion.

[0008] (4) The surface treatment metallic material of the aforementioned (3) publication a phosphoric acid compound and whose phosphoric acid hydride are alt.(hydrogen) phosphoric acid, a metaphosphoric acid compound, polyphosphoric acid (hydrogen) compounds, or such mixture.

(5) The surface treatment metallic material given [aforementioned] in (1) - (4) which contains one sort or two sorts or more of compounds with which a corrosion-resistant enveloping layer is chosen from the oxide, the hydroxide, halogenide, and organic-acid compound of rare earth elements as an addition component.

(6) The surface treatment metallic material of the aforementioned (5) publication whose rare earth elements of an addition component are ceriums.

(7) The surface treatment metallic material given [aforementioned] in (1) - (6) with which a corrosion-resistant enveloping layer contains organic system inhibitor further as an addition component.

[0009] Organic system inhibitor (8) The formylation derivative of an N-phenyl-dimethyl pyrrole, The thioglycolic acid ester expressed with $\text{HS-CH}_2\text{COOCnH}_{2n+1}$ (n is the integer of 1-25), and its derivative, alpha-mercapto carboxylic acid expressed with $\text{CnH}_{2n}(\text{SH})\text{COOH}$ (n is the integer of 1-25), and its derivative, A quinoline and its derivative, triazine dithiol and its derivative, gallate, and its derivative, It is the surface treatment metallic material of the above (7) which is one sort or two sorts or more of mixture chosen from a nicotinic acid and its derivative, a catechol and its derivative, and/or a conductive polymer.

[0010]

[Embodiment of the Invention] The designation of the compound with oxygen acid anions, such as phosphoric acid ion, tungstic-acid ion, and vanadium acid ion, a rare earth metal element, and/or an IVA group element is carried out to the oxygen acid compound of the rare earth metal element used for this invention, and/or an IVA group element, oxygen acid hydride, or such mixture, and the oxygen acid hydride carries out the designation of the compound which contains hydrogen in a part of cation to them. as the phosphoric acid compound of a lanthanum -- LaPO_4 etc. -- as the phosphoric acid hydride of the lanthanum corresponding to [are and] this -- $\text{La}(\text{H}_2\text{PO}_4)_3$ and $\text{La}_2\text{3}(\text{HPO}_4)$ It is.

[0011] These oxygen acid compound and/or the oxygen acid hydride Since the inorganic polymer of **

amorphous nature (amorphous) is probably formed by the shape of a paste Even if it forms membranes, while having processing flattery nature and controlling corrosion according to the barrier effectiveness Since the passive state coat of an oxygen acid salt coat mold can be formed by making oxygen acid superfluous and the passive state coat of an oxide film mold can be made to form, a corrosion-resistant chemical conversion coat with still higher anti-corrosiveness can be obtained.

[0012] Although it cannot limit since a need addition changes with the corrosion resistance searched for as an amount of the oxygen acid compound of the rare earth elements contained in the coat on a metallic material, and/or an IVA group element, and/or the oxygen acid hydride, it is 1 mg/m² by rare earth and IVA group element metal conversion. What is necessary is just to be above. 1 mg/m² The following of the addition effectiveness is inadequate and the corrosion-resistant improvement as a coat is not accepted by it. Moreover, 10 g/m² When economical efficiency is taken into consideration since the corrosion-resistant improvement effectiveness is saturated even if it exceeds and adds, they are 10 g/m². It is enough.

[0013] An existence-in processing liquid of oxygen acid compound [of rare earth elements and/or an IVA group element] and/or oxygen acid hydride gestalt has desirable colloid which carried out detailed distribution into the dissolved condition or processing liquid, although it is dependent on the solvent used, pH, temperature, and concentration. Except [these], when a coat is formed, the distributed condition of the oxygen acid compound of rare earth elements and/or an IVA group element and/or the oxygen acid hydride may become an ununiformity, and anti-corrosiveness may fall in few places of the abundance of the oxygen acid compound of rare earth elements and/or an IVA group element, and/or the oxygen acid hydride.

[0014] As mean particle diameter at the time of carrying out detailed distribution of the oxygen acid compound and/or oxygen acid hydride of rare earth elements and/or an IVA group element at colloid, 3 micrometers or less are desirable and especially 0.2 micrometers or less are desirable 1 more micrometer or less. There is a problem of the thickness of a coat from which the distributed condition of the oxygen acid compound of the rare earth elements in the inside of processing liquid and a coat and/or an IVA group element and/or the oxygen acid hydride becomes an ununiformity for particle diameter to be 3 micrometers or more being restricted.

[0015] It is not limited especially that what is necessary is just the ingredient which does not spoil remarkably the distributed stability of the oxygen acid compound of the rare earth elements in the inside of processing liquid, and/or an IVA group element, and/or the oxygen acid hydride, and holds physically the oxygen acid compound and/or oxygen acid hydride of rare earth elements and/or an IVA group element to a surface of metal as a resin matrix component used for this invention, and has a metallic material and adhesion. Generally, organic resin, such as acrylic, an epoxy system, and an olefin system, is raised as an example, and can choose suitably emulsion resin, a latex, etc. which were distributed in water solubility and water as a gestalt.

[0016] the weight ratio (the oxygen acid acid compound of rare earth elements and/or an IVA group element, oxygen acid hydride, or these mixture/resin) of the oxygen acid acid compound of the rare earth elements which are the principal components of an enveloping layer, and/or an IVA group element, oxygen acid hydride or such mixture, and resin -- 0.001-1000 -- desirable -- 0.01-100 -- 0.1-10 are still more preferably good. Corrosion resistance is not enough, less than 0.001 are not enough as a mineral constituent, if 1000 is exceeded, a resinous principle is not enough, and improvement in processing flattery nature is not found.

[0017] Surfactants, such as a dispersant and a defoaming agent, and other additives can also be compounded and used for the coat and processing liquid of this invention in addition to organic system inhibitor, a corrosion inhibitor like a cerium compound, and a passivation coat formation assistant. Organic system inhibitor has adsorbent [to a surface of metal], and in order that complexing of it may be carried out and it may catch at the time of the elution of a metal ion, it has the operation which controls the further advance of ionization. As the organic system inhibitor, the compound which has the functional groups (-OH, =NH, -SH, -CHO, -COOH, etc.) in which required functional groups (=O, -NH₂, =NH, =N-, =S, -OH, etc.) and covalent bonding with a surface of metal are possible to metal

complex bonding can be used into the molecular structure. In addition, the inhibitor made to contain in a coat has the desirable compound of difficulty water solubility.

[0018] As this reason, in order to elute easily that it is soluble in order to ***** because organic system inhibitor carries out the minute amount dissolution with the water which penetrates a coat at the time of coat transparency of water and not to demonstrate a function, or since this corrosion depressant action does not have enough durability, it is not desirable. As an example of the organic system inhibitor of difficulty water solubility which has the above-mentioned functional group The formylation derivative of an N-phenyl-dimethyl pyrrole, the thioglycolic acid ester expressed with $\text{HS-CH}_2\text{COOCnH}_{2n+1}$ (n is the integer of 1-25), and its derivative, alpha-mercapto carboxylic acid expressed with $\text{CnH}_{2n}(\text{SH})\text{COOH}$ (n is the integer of 1-25), and its derivative, They are a quinoline and its derivative, triazine dithiol and its derivative, gallate and its derivative, a nicotinic acid and its derivative, a catechol, its derivative, etc.

[0019] An electronic conduction nature conductive polymer can also be used as organic system inhibitor in which a corrosion prevention device differs from these. This is the single molecule of a repeat unit with which the pi electron conjugated bond spread in the whole molecule, and polyacetylene, the poly aniline, the poly thiophene, polypyrrole, etc. are known. Electronic conduction nature can be given by adding a barium sulfate etc. to this as a dopant. Although it is unknown for details about a corrosion prevention operation of this conductive polymer, what discovers the corrosion current rectification-ized operation by the interface and oxygen reduction depressant action by electronic conduction nature, and functions as a cathodic protection agent is presumed.

[0020] in addition, these organic system inhibitor -- one sort -- or -- although two or more sorts use it, mixing -- the addition -- the mole ratio (organic system inhibitor / rare earth elements, and/or IVA group element) of rare earth elements and/or an IVA group element, and organic system inhibitor -- 0.001-2 -- desirable -- 0.01-1 -- it is 0.02-0.5 still more preferably. As for the addition effectiveness, less than 0.001 are not enough as a mole ratio, and adhesion is not enough if 2 is exceeded. Moreover, it can be made to contain in a coat by the approach of after the full dissolution and deionized water being dropped at alcohol, such as ethanol and isopropyl alcohol, making detailed colloid form, and adding in processing liquid, or it makes it dissolve in phosphoric acid beforehand although [it adds as it is, for example in processing liquid and mixes] especially the gestalt of these inhibitor in the inside of a coat is not limited, and it adds in processing liquid.

[0021] the case where a cerium compound still like the oxide of a cerium, a hydroxide, a halogenide, and an organic-acid compound is added -- the mole ratio (a cerium compound / rare earth elements, and/or IVA group element) of the rare earth elements of a matrix and/or an IVA group element, and a cerium compound -- 50 or less -- it is -- desirable -- ten or less -- further -- this -- it is five or less preferably. When exceeding 50, membrane formation nature falls and sufficient processing flattery nature is not obtained. As an amount of ceriums contained in a coat, it is 1 mg/m². What is necessary is just to be above. 1 mg/m² The following is not enough for corrosion resistance. Moreover, 10 g/m² Even if it exceeds, when corrosion resistance does not improve so much but economical efficiency is taken into consideration, it is 10g/m². It is enough.

[0022] as a passivation coat formation assistant -- as phosphoric acid, Pori phosphoric acid, and an additive -- a calcium hydroxide, a calcium carbonate, a calcium oxide, phosphoric acid zinc, a phosphoric acid potassium, calcium phosphate, a calcium silicate, zirconium silicate, phosphoric acid aluminum, a phosphoric acid zirconium, TiO₂, SiO₂, and aluminum 2O₃ etc. -- it can add. The processing liquid for forming the coat of this invention consists of the matrix components and solvents of an oxygen acid compound and/or the oxygen acid hydride, and resin of rare earth elements and/or an IVA group element fundamentally, and especially the concentration or pH of processing liquid are not limited. A solvent can choose either an volatile drainage system or an volatile organic compound. However, the drainage system is more desirable when work environment is taken into consideration.

[0023] It does not limit especially that what is necessary is to apply processing liquid to a metallic material front face, and just to dry as the manufacture approach of the surface treatment metallic material of this invention. For example, a spreading facility of chromate treatment, a paint facility of a

coating, etc. by which current use is carried out can be diverted as it is, and do not need a special facility. Moreover, it can apply manually using brush coating or a bar coating machine, and a coat can also be formed by drying. Although desiccation conditions cannot generally be *****ed), they dry the solvent contained in processing liquid at least, and should just be dried in the temperature requirement which the resin matrix component to contain does not decompose. For example, the range whose metallic material surface attainment temperature is 50 degrees C - 200 degrees C is desirable. Although thickness cannot be limited since it changes by the application, its 0.01 micrometers or more are desirable. It is 0.1 micrometers or more still more preferably. Less than 0.01 micrometers of corrosion resistance are not enough. However, since it is saturated, if economical efficiency is taken into consideration, 10 micrometers is enough as the corrosion-resistant improvement effectiveness, even if thickness exceeds 10 micrometers.

[0024] Although especially the metallic material set as the object of this invention is not limited, it is applicable to metal plates, such as surface treated steel sheets, such as electroplating steel plates, such as a hot-dipping steel plate [, such as a hot-dip zinc-coated carbon steel sheet, a melting zinc-iron alloy plating steel plate, a melting zinc-aluminum magnesium alloy plating steel plate a melting aluminum silicon alloy-plating steel plate, and a molten lead-tin alloy-plating steel plate,], electrolytic-zinc-coated-carbon-steel-sheet and electrolytic zinc-nickel alloy plating steel plate, electrolytic zinc-iron alloy plating steel plate, and electrolytic zinc-chromium alloy plating, cold rolled sheet steel, zinc, aluminum, and magnesium, etc., for example.

[0025] As an example of the manufacture approach of the surface treatment metallic material of this invention, it fully mixes and a lanthanum compound and phosphoric acid are heat-treated (100-200 degrees C, 0.5 - 24 hours), and organic system inhibitor, a cerium compound, etc. are added to the obtained paste-like product, and it fully mixes. These additives can raise corrosion resistance as mentioned above. This processing liquid is applied to a metal plate, and the target surface treatment metallic material is obtained by performing desiccation and heat treatment (100-200 degrees C of board temperature, for [30 seconds] - 1 hour).

[0026]

[Example]

The mineral constituent LP of the method-of-preparation (1) matrix of processing liquid: After fully mixing 115.3g (85%) of phosphoric acid with 32.6g of lanthanum trioxides, it heated at 150 degrees C for 12 hours.

CP: After fully mixing phosphoric acid cerium 23.5g and 115.3g (85%) of phosphoric acid, it heated at 150 degrees C for 12 hours.

YP: After fully mixing 115.3g (85%) of phosphoric acid with 30.3g of yttrium chlorides, it heated at 150 degrees C for 12 hours.

NP: After fully mixing 39.6g of neodymium chlorides, and 115.3g (85%) of phosphoric acid, it heated at 150 degrees C for 12 hours.

[0027] LPP: After fully mixing 338g (average molecular weight 338) of polyphosphoric acid with 32.6g of lanthanum trioxides, it heated at 150 degrees C for 12 hours.

LW: After fully mixing 261.0g (4%) of tungstic-acid ammonium water solutions with 32.6g of lanthanum trioxides, it heated at 150 degrees C for 12 hours.

LM: After fully mixing 176.6g (28%) of ammonium-molybdate water solutions with 32.6g of lanthanum oxide, it heated at 150 degrees C for 12 hours.

[0028] LV: After fully mixing 117.0g (5%) of ammonium-vanadate water solutions with 32.6g of lanthanum oxide, respectively, it heated at 150 degrees C for 12 hours.

ZP: After fully mixing with 100g (32%) of chlorination zirconium dioxide water solutions, and 115.3g (85%) of phosphoric acid, it heated at 150 degrees C for 12 hours.

TP: After fully mixing with 100g (24%) of sulfuric-acid titanium water solutions, and 115.3g (85%) of phosphoric acid, it heated at 150 degrees C for 12 hours.

[0029] (2) The resinous principle block copolymer of a matrix (it considers as Following AR) : the Pori (methacrylic-acid, hydroxyethyl acrylate, hydroxyethyl methacrylate)-Pori (styrene, methyl-

methacrylate, methacrylic-acid butyl, butyl acrylate)-Pori (methacrylic-acid, hydroxyethyl acrylate, hydroxyethyl methacrylate) block copolymer (solvent: tetrahydrofuran) was manufactured by the living anionic polymerization method. An acrylic emulsion (it considers as Following BR): Commercial water-dispersion carboxyl group content acrylic emulsion resin (Japan Synthetic Rubber [Co., Ltd.] make: 50 % of the weight of resin solid content) was used.

[0030] SBR latex (it considers as Following CR): The commercial moisture powder carboxyl group content SBR latex (Japan Synthetic Rubber [Co., Ltd.] make: 50 % of the weight of resin solid content) was used. The initial make-up of electrolytic bath of the above-mentioned rare earth and/or the oxygen acid (hydrogen) compound of an IVA group element, resin, and the various additives was blended and carried out (Tables 1-8). Moreover, in 200g/l and colloidal silica addition, initial-make-up-of-electrolytic-bath concentration is SiO₂ with the oxygen acid compound and/or the oxygen acid hydride (rare earth, IVA group element metal conversion), and resin (solid content conversion) of rare earth elements and/or an IVA group element. In 5 g/l and cerium compound addition, in 10 g/l and organic system inhibitor addition, it unified into the conditions of 10 g/l by conversion. In addition, it compounded about alpha-mercapto lauryl acid and the commercial reagent was used about the other thing (the dopant of the poly aniline water solution is a barium sulfate in a 1-% of the weight water solution).

[0031] The processing liquid of the coat forming method tables 1-8 was applied so that a bar coating machine might be used and the coat thickness after desiccation might be set to 1 micrometer on a metal plate, and it was heat-treated for 1 minute at 100 degrees C of board temperature. The used metallic materials are GI (a hot-dip zinc-coated carbon steel sheet and plating coating weight:90 g/m²), EG (an electrolytic zinc-coated carbon steel sheet and plating coating weight:20 g/m²), and aluminum (a melting aluminum silicon alloy-plating steel plate, plating coating weight: 120g/m², aluminum/Si=90/10). In addition, it is a partial reduction chromic acid according to starch as chromate treatment liquid in order to perform the comparison with a chromate treatment steel plate CrO₃ It is 30 g/l and SiO₂ by conversion. Carried out the initial make-up of electrolytic bath of the processing bath which carries out 20 g/l content of 40 g/l and the phosphoric acid, it was made to apply, dry and harden on a steel plate, and coat formation was performed (the amount of Cr(s) in a coat is converted into Metal Cr, and is 100 gm/m²).

[0032] the performance-evaluation method (a) sample of a coat -- Erichsen 7.5mm -- SEM observation was performed after processing and processing flattery nature evaluation was performed.

評点 ◎ : 亀裂なし

○ : 微小亀裂

△ : 微小剥離

× : 大亀裂、大面積剥離

[0033] (b) Monotonous corrosion resistance evaluation was performed in the rust generating area after spraying 35-degree C salt water on a sample 5%. In addition, in 18 days, all, GI and EG measured by the white rust incidence rate in 12 days, and aluminum measured the spraying period.

評点 ◎ : 錆発生率 0 %

○ : 錆発生率 5 %未満

△ : 錆発生率 5 %以上、20 %未満

× : 錆発生率 20 %以上

[0034] (c) a sample -- Erichsen 7mm -- processing section corrosion resistance evaluation was performed after processing in the rust generating area after spraying 35-degree C salt water 5%. In addition, in 18 days, all, GI and EG measured by the white rust incidence rate in 12 days, and aluminum measured the spraying period.

評点 ◎：錆発生率 0 %
○：錆発生率 5 %未満
△：錆発生率 5 %以上、20 %未満
×：錆発生率 20 %以上

The surface treatment metal material of this invention was excellent in processing flattery nature and coating adhesion, and showed a plate equivalent to chromate treatment, and processing section corrosion resistance so that clearly from these evaluation results (Tables 1-8). Therefore, it considers as the chemical conversion film which does not contain hexavalent chromium at all, and excels in environmental compatibility upwards, and the effectiveness is demonstrated as a corrosion-resistant coat.

[0035]

[Table 1]

表 1

No	マトリックス			セリウム化合物	添加物	金属板	加工追従性	耐食性		備考
	無機成分	樹脂成分	比率 (無機：樹脂)					平板	加工部	
1	LP	AR	90:10	-	-	GI	△～○	○	△～○	実施例
2	LP	AR	50:50	-	-	GI	○	○	○	
3	LP	AR	50:50	-	-	EG	○	○	○	
4	LP	AR	50:50	-	-	AL	○	○	○	
5	LP	AR	50:50	-	シリカ	GI	○	◎	○～◎	
6	LP	AR	50:50	酸化セリウム	-	GI	○	◎	○～◎	
7	LP	AR	50:50	水酸化セリウム	-	GI	○	◎	○～◎	
8	LP	AR	50:50	塩化セリウム	-	GI	○	◎	○～◎	
9	LP	AR	50:50	珪酸セリウム	-	GI	○	◎	○～◎	
10	LP	AR	10:90	-	-	GI	◎	△	△	比較例
11	LP	AR	100:0	-	-	GI	△	○	△	
12	LP	AR	0:100	-	-	GI	◎	×	×	実施例
13	LP	BR	90:10	-	-	GI	△～○	○	△～○	
14	LP	BR	50:50	-	-	GI	○	○	○	
15	LP	BR	50:50	-	-	EG	○	○	○	
16	LP	BR	50:50	-	-	AL	○	○	○	
17	LP	BR	50:50	-	シリカ	GI	○	◎	○～◎	
18	LP	BR	50:50	酸化セリウム	-	GI	○	◎	○～◎	
19	LP	BR	50:50	水酸化セリウム	-	GI	○	◎	○～◎	
20	LP	BR	50:50	塩化セリウム	-	GI	○	◎	○～◎	
21	LP	BR	50:50	珪酸セリウム	-	GI	○	◎	○～◎	
22	LP	BR	10:90	-	-	GI	◎	△	△	比較例
23	LP	BR	100:0	-	-	GI	△	○	△	
24	LP	BR	0:100	-	-	GI	◎	×	×	実施例
25	LP	CR	90:10	-	-	GI	△～○	○	△～○	
26	LP	CR	50:50	-	-	GI	○	○	○	
27	LP	CR	50:50	-	-	EG	○	○	○	
28	LP	CR	50:50	-	-	AL	○	○	○	
29	LP	CR	50:50	-	シリカ	GI	○	◎	○～◎	
30	LP	CR	50:50	酸化セリウム	-	GI	○	◎	○～◎	
31	LP	CR	50:50	水酸化セリウム	-	GI	○	◎	○～◎	
32	LP	CR	50:50	塩化セリウム	-	GI	○	◎	○～◎	
33	LP	CR	50:50	珪酸セリウム	-	GI	○	◎	○～◎	
34	LP	CR	10:90	-	-	GI	◎	△	△	比較例
35	LP	CR	100:0	-	-	GI	△	○	△	
36	LP	CR	0:100	-	-	GI	◎	×	×	比較例

[0036]

[Table 2]

表 2

No	マトリックス			セリウム化合物	添加物	金属板	加工追従性	耐 食 性		備 考
	無機成分	樹脂成分	比 率 (無機：樹脂)					平板	加工部	
37	CP	AR	90:10	—	—	GI	△～○	○	△～○	実施例
38	CP	AR	50:50	—	—	GI	○	○	○	
39	CP	AR	50:50	—	—	EG	○	○	○	
40	CP	AR	50:50	—	—	AL	○	○	○	
41	CP	AR	50:50	—	シリカ	GI	○	◎	○—○	
42	CP	AR	50:50	酸化セリウム	—	GI	○	◎	○—○	
43	CP	AR	50:50	水酸化セリウム	—	GI	○	◎	○—○	
44	CP	AR	50:50	塩化セリウム	—	GI	○	◎	○—○	
45	CP	AR	50:50	蓚酸セリウム	—	GI	○	◎	○—○	
46	CP	AR	10:90	—	—	GI	◎	△	△	比較例
47	CP	AR	100:0	—	—	GI	△	○	△	
48	CP	AR	0:100	—	—	GI	◎	×	×	実施例
49	CP	BR	90:10	—	—	GI	△～○	○	△～○	
50	CP	BR	50:50	—	—	GI	○	○	○	
51	CP	BR	50:50	—	—	EG	○	○	○	
52	CP	BR	50:50	—	—	AL	○	○	○	
53	CP	BR	50:50	—	シリカ	GI	○	◎	○—○	
54	CP	BR	50:50	酸化セリウム	—	GI	○	◎	○—○	
55	CP	BR	50:50	水酸化セリウム	—	GI	○	◎	○—○	
56	CP	BR	50:50	塩化セリウム	—	GI	○	◎	○—○	
57	CP	BR	50:50	蓚酸セリウム	—	GI	○	◎	○—○	
58	CP	BR	10:90	—	—	GI	◎	△	△	比較例
59	CP	BR	100:0	—	—	GI	△	○	△	
60	CP	BR	0:100	—	—	GI	◎	×	×	実施例
61	CP	CR	90:10	—	—	GI	△～○	○	△～○	
62	CP	CR	50:50	—	—	GI	○	○	○	
63	CP	CR	50:50	—	—	EG	○	○	○	
64	CP	CR	50:50	—	—	AL	○	○	○	
65	CP	CR	50:50	—	シリカ	GI	○	◎	○—○	
66	CP	CR	50:50	酸化セリウム	—	GI	○	◎	○—○	
67	CP	CR	50:50	水酸化セリウム	—	GI	○	◎	○—○	
68	CP	CR	50:50	塩化セリウム	—	GI	○	◎	○—○	
69	CP	CR	50:50	蓚酸セリウム	—	GI	○	◎	○—○	
70	CP	CR	10:90	—	—	GI	◎	△	△	比較例
71	CP	CR	100:0	—	—	GI	△	○	△	
72	CP	CR	0:100	—	—	GI	◎	×	×	比較例

[0037]

[Table 3]

表 3

No	マトリックス			セリウム化合物	添加物	金属板	加工追従性	耐 食 性		備 考
	無機成分	樹脂成分	比 率 (無機：樹脂)					平板	加工部	
73	YP	AR	90:10	—	—	GI	△～○	○	△～○	実 施 例
74	YP	AR	50:50	—	—	GI	○	○	○	
75	YP	AR	50:50	—	—	EG	○	○	○	
76	YP	AR	50:50	—	—	AL	○	○	○	
77	YP	AR	50:50	—	シリカ	GI	○	◎	○～◎	
78	YP	AR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
79	YP	AR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
80	YP	AR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
81	YP	AR	50:50	砒酸セリウム	—	GI	○	◎	○～◎	
82	YP	AR	10:90	—	—	GI	◎	△	△	比 較 例
83	YP	AR	100:0	—	—	GI	△	○	△	
84	YP	AR	0:100	—	—	GI	◎	×	×	実 施 例
85	YP	BR	90:10	—	—	GI	△～○	○	△～○	
86	YP	BR	50:50	—	—	GI	○	○	○	
87	YP	BR	50:50	—	—	EG	○	○	○	
88	YP	BR	50:50	—	—	AL	○	○	○	
89	YP	BR	50:50	—	シリカ	GI	○	◎	○～◎	
90	YP	BR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
91	YP	BR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
92	YP	BR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
93	YP	BR	50:50	砒酸セリウム	—	GI	○	◎	○～◎	
94	YP	BR	10:90	—	—	GI	◎	△	△	比 較 例
95	YP	BR	100:0	—	—	GI	△	○	△	
96	YP	BR	0:100	—	—	GI	◎	×	×	実 施 例
97	YP	CR	90:10	—	—	GI	△～○	○	△～○	
98	YP	CR	50:50	—	—	GI	○	○	○	
99	YP	CR	50:50	—	—	EG	○	○	○	
100	YP	CR	50:50	—	—	AL	○	○	○	
101	YP	CR	50:50	—	シリカ	GI	○	◎	○～◎	
102	YP	CR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
103	YP	CR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
104	YP	CR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
105	YP	CR	50:50	砒酸セリウム	—	GI	○	◎	○～◎	
106	YP	CR	10:90	—	—	GI	◎	△	△	比 較 例
107	YP	CR	100:0	—	—	GI	△	○	△	
108	YP	CR	0:100	—	—	GI	◎	×	×	比 較 例

[0038]

[Table 4]

表 4

No	マトリックス			セリウム化合物	添加物	金属板	加工追従性	耐 食 性		備考
	無機成分	樹脂成分	比 率 (無機:樹脂)					平板	加工部	
109	NP	AR	90:10	—	—	GI	△~○	○	△~○	実施例
110	NP	AR	50:50	—	—	GI	○	○	○	
111	NP	AR	50:50	—	—	EG	○	○	○	
112	NP	AR	50:50	—	—	AL	○	○	○	
113	NP	AR	50:50	—	シリカ	GI	○	◎	○~◎	
114	NP	AR	50:50	酸化セリウム	—	GI	○	◎	○~◎	
115	NP	AR	50:50	水酸化セリウム	—	GI	○	◎	○~◎	
116	NP	AR	50:50	塩化セリウム	—	GI	○	◎	○~◎	
117	NP	AR	50:50	砒酸セリウム	—	GI	○	◎	○~◎	
118	NP	AR	10:90	—	—	GI	◎	△	△	比較例
119	NP	AR	100:0	—	—	GI	△	○	△	
120	NP	AR	0:100	—	—	GI	◎	×	×	実施例
121	NP	BR	90:10	—	—	GI	△~○	○	△~○	
122	NP	BR	50:50	—	—	GI	○	○	○	
123	NP	BR	50:50	—	—	EG	○	○	○	
124	NP	BR	50:50	—	—	AL	○	○	○	
125	NP	BR	50:50	—	シリカ	GI	○	◎	○~◎	
126	NP	BR	50:50	酸化セリウム	—	GI	○	◎	○~◎	
127	NP	BR	50:50	水酸化セリウム	—	GI	○	◎	○~◎	
128	NP	BR	50:50	塩化セリウム	—	GI	○	◎	○~◎	
129	NP	BR	50:50	砒酸セリウム	—	GI	○	◎	○~◎	
130	NP	BR	10:90	—	—	GI	◎	△	△	比較例
131	NP	BR	100:0	—	—	GI	△	○	△	
132	NP	BR	0:100	—	—	GI	◎	×	×	実施例
133	NP	CR	90:10	—	—	GI	△~○	○	△~○	
134	NP	CR	50:50	—	—	GI	○	○	○	
135	NP	CR	50:50	—	—	EG	○	○	○	
136	NP	CR	50:50	—	—	AL	○	○	○	
137	NP	CR	50:50	—	シリカ	GI	○	◎	○~◎	
138	NP	CR	50:50	酸化セリウム	—	GI	○	◎	○~◎	
139	NP	CR	50:50	水酸化セリウム	—	GI	○	◎	○~◎	
140	NP	CR	50:50	塩化セリウム	—	GI	○	◎	○~◎	
141	NP	CR	50:50	砒酸セリウム	—	GI	○	◎	○~◎	
142	NP	CR	10:90	—	—	GI	◎	△	△	比較例
143	NP	CR	100:0	—	—	GI	△	○	△	
144	NP	CR	0:100	—	—	GI	◎	×	×	比較例

[0039]

[Table 5]

表 5

No	マトリックス			セリウム化合物	添加物	金属板	加工追従性	耐 食 性		備 考
	無機成分	樹脂成分	比 率 (無機：樹脂)					平板	加工部	
145	ZP	AR	90:10	—	—	GI	△～○	○	△～○	実 施 例
146	ZP	AR	50:50	—	—	GI	○	○	○	
147	ZP	AR	50:50	—	—	EG	○	○	○	
148	ZP	AR	50:50	—	—	AL	○	○	○	
149	ZP	AR	50:50	—	シリカ	GI	○	◎	○～◎	
150	ZP	AR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
151	ZP	AR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
152	ZP	AR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
153	ZP	AR	50:50	硫酸セリウム	—	GI	○	◎	○～◎	
154	ZP	AR	10:90	—	—	GI	◎	△	△	比 較 例
155	ZP	AR	100:0	—	—	GI	△	○	△	
156	ZP	AR	0:100	—	—	GI	◎	×	×	実 施 例
157	ZP	BR	90:10	—	—	GI	△～○	○	△～○	
158	ZP	BR	50:50	—	—	GI	○	○	○	
159	ZP	BR	50:50	—	—	EG	○	○	○	
160	ZP	BR	50:50	—	—	AL	○	○	○	
161	ZP	BR	50:50	—	シリカ	GI	○	◎	○～◎	
162	ZP	BR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
163	ZP	BR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
164	ZP	BR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
165	ZP	BR	50:50	硫酸セリウム	—	GI	○	◎	○～◎	
166	ZP	BR	10:90	—	—	GI	◎	△	△	比 較 例
167	ZP	BR	100:0	—	—	GI	△	○	△	
168	ZP	BR	0:100	—	—	GI	◎	×	×	実 施 例
169	ZP	CR	90:10	—	—	GI	△～○	○	△～○	
170	ZP	CR	50:50	—	—	GI	○	○	○	
171	ZP	CR	50:50	—	—	EG	○	○	○	
172	ZP	CR	50:50	—	—	AL	○	○	○	
173	ZP	CR	50:50	—	シリカ	GI	○	◎	○～◎	
174	ZP	CR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
175	ZP	CR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
176	ZP	CR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
177	ZP	CR	50:50	硫酸セリウム	—	GI	○	◎	○～◎	
178	ZP	CR	10:90	—	—	GI	◎	△	△	比 較 例
179	ZP	CR	100:0	—	—	GI	△	○	△	
180	ZP	CR	0:100	—	—	GI	◎	×	×	比 較 例

[0040]

[Table 6]

表 6

No	マトリックス			セリウム化合物	添加物	金属板	加工追従性	耐 食 性		備 考
	無機成分	樹脂成分	比 率 (無機 : 樹脂)					平板	加工部	
181	TP	AR	90:10	—	—	GI	△～○	○	△～○	実 施 例
182	TP	AR	50:50	—	—	GI	○	○	○	
183	TP	AR	50:50	—	—	EG	○	○	○	
184	TP	AR	50:50	—	—	AL	○	○	○	
185	TP	AR	50:50	—	シリカ	GI	○	◎	○～◎	
186	TP	AR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
187	TP	AR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
188	TP	AR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
189	TP	AR	50:50	萆酸セリウム	—	GI	○	◎	○～◎	
190	TP	AR	10:90	—	—	GI	◎	△	△	比 較 例
191	TP	AR	100:0	—	—	GI	△	○	△	
192	TP	AR	0:100	—	—	GI	◎	×	×	実 施 例
193	TP	BR	90:10	—	—	GI	△～○	○	△～○	
194	TP	BR	50:50	—	—	GI	○	○	○	
195	TP	BR	50:50	—	—	EG	○	○	○	
196	TP	BR	50:50	—	—	AL	○	○	○	
197	TP	BR	50:50	—	シリカ	GI	○	◎	○～◎	
198	TP	BR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
199	TP	BR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
200	TP	BR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
201	TP	BR	50:50	萆酸セリウム	—	GI	○	◎	○～◎	
202	TP	BR	10:90	—	—	GI	◎	△	△	比 較 例
203	TP	BR	100:0	—	—	GI	△	○	△	
204	TP	BR	0:100	—	—	GI	◎	×	×	実 施 例
205	TP	CR	90:10	—	—	GI	△～○	○	△～○	
206	TP	CR	50:50	—	—	GI	○	○	○	
207	TP	CR	50:50	—	—	EG	○	○	○	
208	TP	CR	50:50	—	—	AL	○	○	○	
209	TP	CR	50:50	—	シリカ	GI	○	◎	○～◎	
210	TP	CR	50:50	酸化セリウム	—	GI	○	◎	○～◎	
211	TP	CR	50:50	水酸化セリウム	—	GI	○	◎	○～◎	
212	TP	CR	50:50	塩化セリウム	—	GI	○	◎	○～◎	
213	TP	CR	50:50	萆酸セリウム	—	GI	○	◎	○～◎	
214	TP	CR	10:90	—	—	GI	◎	△	△	比 較 例
215	TP	CR	100:0	—	—	GI	△	○	△	
216	TP	CR	0:100	—	—	GI	◎	×	×	
217	クロート皮膜					GI	△	◎	△	
218	クロート皮膜					EG	△	◎	△	
219	クロート皮膜					AL	△	◎	△	

[0041]

[Table 7]

表 7

No	マトリックス			セリウム化合物	有機系インヒビター	金属板	加工追従性	耐食性		備考
	無機	樹脂	比率					平板	加工部	
1	LP	AR	50:50	酸化セリウム	チオグリコール酸ブチル	GI	○	◎	◎	実 施 例
2	LP	AR	50:50	—	チオグリコール酸ブチル	GI	○	◎	○—○	
3	LP	AR	50:50	酸化セリウム	8-メルカプトキノリン	GI	○	◎	◎	
4	LP	AR	50:50	—	8-メルカプトキノリン	GI	○	◎	○—○	
5	LP	AR	50:50	酸化セリウム	ポリアニリン水溶液	GI	○	◎	◎	
6	LP	AR	50:50	—	ポリアニリン水溶液	GI	○	◎	○—○	
7	LP	AR	50:50	酸化セリウム	α -メルカプトラウリル酸	GI	○	◎	◎	
8	LP	AR	50:50	—	α -メルカプトラウリル酸	GI	○	◎	○—○	
9	LP	AR	50:50	酸化セリウム	ニコチン酸	GI	○	◎	◎	
10	LP	AR	50:50	—	ニコチン酸	GI	○	◎	○—○	
11	LP	AR	50:50	酸化セリウム	カテコール	GI	○	◎	◎	
12	LP	AR	50:50	—	カテコール	GI	○	◎	○—○	
13	LPP	AR	50:50	酸化セリウム	チオグリコール酸ブチル	GI	○	◎	◎	
14	LPP	AR	50:50	—	チオグリコール酸ブチル	GI	○	◎	○—○	
15	LPP	AR	50:50	酸化セリウム	8-メルカプトキノリン	GI	○	◎	◎	
16	LPP	AR	50:50	—	8-メルカプトキノリン	GI	○	◎	○—○	
17	LPP	AR	50:50	酸化セリウム	ポリアニリン水溶液	GI	○	◎	◎	
18	LPP	AR	50:50	—	ポリアニリン水溶液	GI	○	◎	○—○	
19	LPP	AR	50:50	酸化セリウム	α -メルカプトラウリル酸	GI	○	◎	◎	
20	LPP	AR	50:50	—	α -メルカプトラウリル酸	GI	○	◎	○—○	
21	LPP	AR	50:50	酸化セリウム	ニコチン酸	GI	○	◎	◎	
22	LPP	AR	50:50	—	ニコチン酸	GI	○	◎	○—○	
23	LPP	AR	50:50	酸化セリウム	カテコール	GI	○	◎	◎	
24	LPP	AR	50:50	—	カテコール	GI	○	◎	○—○	

[0042]

[Table 8]

表 8

No	マトリックス			金属板	加工追従性	耐食性		備考
	無機成分	樹脂成分	比率（無機：樹脂）			平板	加工部	
1	LW	AR	50:50	GI	○	○	○	実施例
2	LW	AR	50:50	EG	○	○	○	
3	LW	AR	50:50	AL	○	○	○	
4	LM	BR	50:50	GI	○	○	○	
5	LM	BR	50:50	EG	○	○	○	
6	LM	BR	50:50	AL	○	○	○	
7	LV	CR	50:50	GI	○	○	○	
8	LV	CR	50:50	EG	○	○	○	
9	LV	CR	50:50	AL	○	○	○	

[0043]

[Effect of the Invention] As stated above, the oxygen acid compound of rare earth elements and/or an IVA group element, the oxygen acid hydride or the coat formed with these mixture and resin, and the coat which contains organic system inhibitor and/or a cerium compound further show the anti-corrosiveness more than high processing flattery nature, the coat containing hexavalent chromium, and an EQC, and does so the effectiveness which combined also with environmental compatibility and was extremely excellent.

[Translation done.]

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